1-Octanol/Water Partition Coefficient of Ionic Liquids

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Abstract

Room temperature ionic liquids are nonvolatile, they can only disperse into the aquatic environment. 1-octanol-water partition coefficient is a measure of the bioconcentration tendency of a chemical in a hydrologic cycle. In this work, 1-octanol-water partition coefficient of 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF_6]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) at 303 K were measured using ultraviolet spectrometer and Karl-Fischer analysis. The 1-octanol/water partition coefficients of [emim][PF_6] measured range from 0.012 to 0.015 when saturated; and those of [bmim][PF_6] obtained are between 0.005 to 0.020. Both sets of values are much smaller than most common organic solvents.

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1. Introduction

In recent years, room temperature ionic liquids have received a lot of attention as the potential "green" and "designer" solvents of the next generation[1], [2].   There have been some related studies in the literature on liquid-liquid phase behavior of ionic liquids in various solvents. Abraham et al.[3] reported the partition coefficients of several organic compounds between 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and water. Selvan et al.[4] recently reported liquid-liquid equilibrium data of 1-ethyl-3-methylimidazolium tri-iodide ([emim][I3]) with toluene and n-heptane by the help of NMR analysis. Dullius et al.[5] shown that tetrafluoroborate-containing ionic liquid display miscibility curves with water typical of a partially miscible two-component system with a upper critical point at 278 K. Swatloski et al.[6] obtained the phase diagram of [bmim][PF_6]+ water+ethanol system phase diagram and found that there are two miscibility gaps. Fadeev et al.[7] used weighting method to measure distribution of butanol between [bmim][PF_6] /1-octyl-3-methylimidazolium ([omim][PF_6]) and water to investigate the use of ionic liquid to recover butanol from fermentation broth. Recently, Heintz et al.[8] presented binary liquid-liquid equilibria data of 1-propanol, 1-butanol and 1-pentanol with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and detected the point of splitting by light scattering. Wu et al.[9] reported binoidal coexistence curves of 1-butanol mixed with 1-alkyl-3-methyl-imidazolium hexafluorophosphate. Anthony et al. [10] measured

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vapor-liquid and liquid-liquid equilibrium of water and three ionic liquids. Huddleston et al.[11] measured the partition coefficient of several substituted aryl chemicals between water and [bmim][PF$_6$] to demonstrate that ionic liquids may be suitable solvents for volatile organics.

Since most of the room temperature ionic liquids are stable and nonvolatile, they can only disperse into the aquatic environment in their widespread applications. Wong et al.[12] measured the solubility of [bmim][PF$_6$] and [emim][PF$_6$] in water are approximately 2.7wt% at 303 K and 4.5wt% at 308 K respectively. Anthony et al. [10] reported solubility values for [bmim][PF$_6$] (2.2 wt%), [C8min][PF$_6$] (0.7 wt%) and [C8min][BF$_4$] (1.8 wt%) at 295 K. These values, while small, are not negligible. Once lost in water, the chemical will accumulate in life-forms can be concentrated up the food chain if it has a high tendency to be retained by fatty tissues. 1-octanol-water partition coefficient is a measure of the bioconcentration and soil sedimentation tendencies of a chemical in a hydrologic cycle[13],[14]. The 1-octanol/water partition coefficient (K_{ow}) is defined as the ratio of molar concentrations (C) of a chemical in 1-octanol and water in dilute solution[15]. If we assume that addition of ionic liquids has no effect on the density of the fluid, the 1-octanol/water partition coefficient can be calculated from the equilibrium weight fractions (w) of the two phases:

$$K_{i,OW} \equiv \frac{C_i^o}{C_i^w} \approx \frac{w_i^o}{w_i^w}\frac{1-w_i^w}{1-w_i^o}\frac{\rho^o}{\rho^w} \tag{1}$$

The superscripts o and w represent the 1-octanol phase and water phase resepctively. ρ is the density of the phase. In this work, we shall report our measurements of 1-octanol-water partition coefficient of 1-ethyl-3-methylimidazolium hexafluorophos -phate ([emim][PF$_6$]), and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) using ultraviolet spectrometer and Karl-Fischer analysis at 303K.

2. Experiments

Ionic reagents [emim][PF$_6$] was obtained from TCI Co. (Tokyo, Japan) with purity greater than 97%. [Bmim][PF$_6$] was obtained from Solvent Innovation GmbH with purity greater than 98%. Both these ionic liquids were kept in desiccator and used without further purification. Reagent grade 1-octanol (purity >99 wt%, water contents less than 0.3wt%) was obtained from Pharmco. 1-Octanol was dehydrated before use in the binary liquid-liquid experiment with ionic liquids.

Solid-liquid and liquid-liquid equilibrium experiments were carried out in a constant temperature water bath (Firstek Scientific B402D), capable of maintaining temperature to within 0.1 K in the range of 303 to 433 K. Temperature of the bath during the experiment was monitored independently using a thermocouple (accuracy ±0.1 K). Preliminary studies were carried out to measure the solubility of ionic liquid in a mixture of 1-octanol+water. We prepared a specific composition of 1-octanol and de-ionized water in a sample bottle placed in a constant water bath. Then [emim][PF$_6$] or [bmim][PF$_6$] was added in small increments until an extra solid or an extra liquid phase appeared. The solvent mixture was added in small increments until the extra phase re-dissolve. The process was repeated several times to determine the SLL or LLL equilibrium limits.

To obtain the 1-octanol/water partition coefficients, liquid-liquid equilibrium tie line compositions were measured. Various amounts of ionic liquids, less than the saturated values, were added to 1-octanol/water mixtures. The mixtures were shaken on a vortex mixer for one minute then kept in a constant temperature bath at 303 K for at least three days and up to nine days when the total composition is closed to the saturated line. Samples of saturated aqueous phase and 1-octanol phase were taken from the mixture and placed in sample vials ready for concentration measurements. Water in the 1-octanol phase was measured using a Karl-Fischer analyzer (Metrohm 701 KF Titrino). Concentrations of ionic liquid were measured using ultraviolet absorption spectroscopy, the maximum wavelengths are 213 nm for [emim][PF$_6$] and 216 nm for [bmim][PF$_6$] which match the reported value of 210 nm by Carda-Broch[16]. The ultraviolet spectrometer was made by Shimadzu, UV-1201.

The solubility of 1-octanol in water, as listed in DECHEMA chemistry data series[17], is barely observable (weight fraction < 1.0×10^{-3}). Since there is no observable difference between ultraviolet responses obtained using water only and water saturated with 1-octanol, we assumed that the analysis was not interfered by traces of 1-octanol.

For the 1-octanol phase, the ultraviolet absorption of ionic liquid is interfered by water. Figure 1 shows the calibration curves of [emim][PF$_6$] in 1-octanol phase at water contents of 0 and 3 wt%. The higher the water content, the lower is the absorption of ultraviolet. In order to determine the ionic liquid concentration in 1-octanol phase, the amount of water in a 1-octanol sample taken from the equilibrium cell was first measured using Karl-Fischer analysis. Once the composition of water in 1-octanol phase was determined, we prepared a standard 1-octanol solution, which contained the exact amount of water measured by Karl-Fischer analysis. Various known amounts of [emim][PF$_6$] were added to this standard solution. A calibration curve at this specific water content was then obtained. Given this calibration curve, the absorption of 1-octanol samples taken from the equilibrium cell was then measured to obtain the [emim][PF$_6$] concentration.
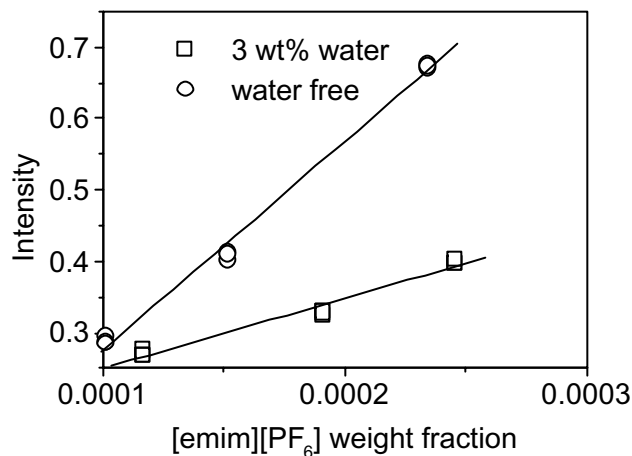

Figure 1: The calibration curve of [emim] [PF$_6$] solved in 1-octanol with different weight fraction of water.

3. Results

The solubility of [emim][PF$_6$] in 1-octanol+water is shown in Figure 2. It was found that the solubility decreases with the additional of 1-octanol. This indicates that the solubility of [emim][PF$_6$] in 1-octanol is less that of [emim][PF$_6$] in water. The equilibrium tie-line compositions measured listed were listed in Table 1. The 1-octanol/water partition coefficient measured ranges from 0.012 to 0.015 as the concentration of [emim][PF$_6$] increases. Therefore the 1-octanol/water partition coefficient should be less than or equal to 0.015 at infinite dilution.
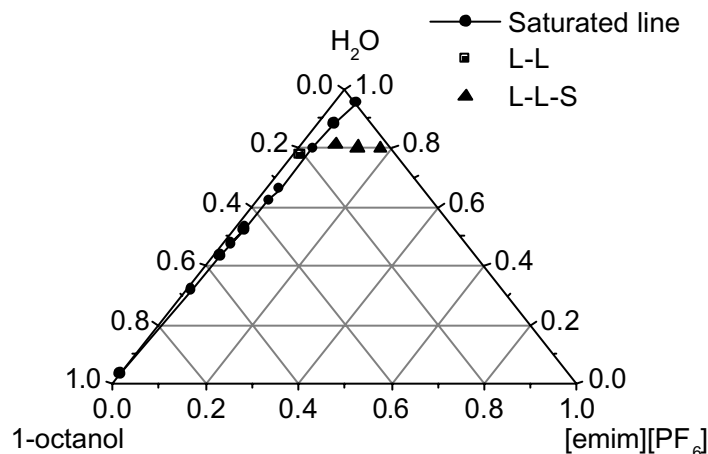

Figure 2. Solubility of [emim][PF$_6$] in 1-octanol+water at 303 K

Table 1. Equilibrium compositions in weight percent and [emim][PF$_6$] partition coefficient in 1-octanol/water. *Kow* is calculated by equation (1)

Aqueous phase		1-octanol phase		
[emim][PF$_6$]	H$_2$O	[emim][PF$_6$]	H$_2$O	K_{ow}
1.0	99.0	0.014	4.65	0.012
2.0	98.0	0.031	4.68	0.013
2.9	97.1	0.048	4.68	0.013
4.0	96.0	0.074	4.70	0.015

[Bmim][PF$_6$] is much difficult to solve in 1-octanol+water than [emim][PF$_6$] and its solubility in 1-octanol+water is shown in Figure 3. The solubility of [bmim][PF$_6$] in pure water is about 2.7w%. Table 2 shows their equilibrium compositions in the liquid-liquid phase region. The last four equilibrium compositions in Table 2 are in saturated state because small amount of third liquid phase was observed. All these samples stayed in constant temperature water bath for nine days, the experimental data show they do reach the saturated and equilibrium state. The 1-octanol/water partition coefficients of [bmim][PF$_6$] measured range from 0.005 to 0.020 and should be less than 0.005 at infinite dilution. Figure 4 shows the feed compositions do ky on their tie lines except the last three samples over the saturation limit.
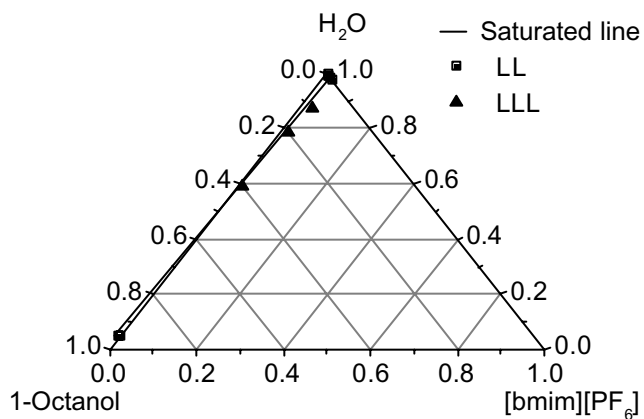
Figure 3. Phase equilibrium of [bmim][PF$_6$] in 1-octanol+water at 303 K

Table 2. Equilibrium compositions and 1-octanol/water partition coefficient of [bmim][PF$_6$]. The data marked by asterisk are in saturated condition.

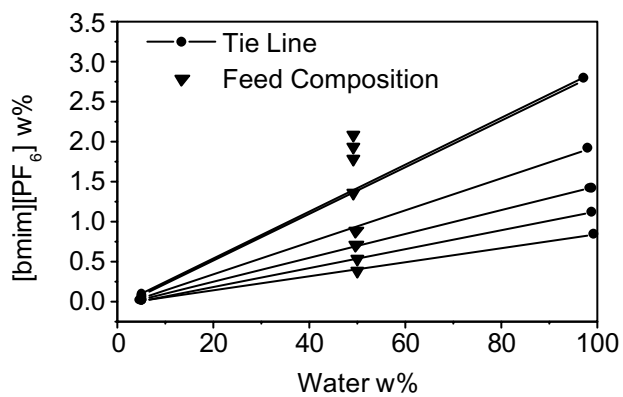| Aqueous phase		1-octanol phase		
[bmim][PF$_6$]	H$_2$O	[bmim][PF$_6$]	H$_2$O	Kow
0.83	99.17	0.005	4.98	0.005
1.12	98.88	0.009	4.99	0.007
1.42	98.58	0.012	4.89	0.007
1.92	98.08	0.021	4.95	0.009
*2.79	97.21	0.060	4.95	0.018
*2.79	97.21	0.065	4.91	0.020
*2.77	97.23	0.065	4.97	0.020
*2.77	97.23	0.064	4.99	0.020

Figure 4. Phase equilibrium of [bmim][PF$_6$] in 1-octanol+water at 303 K

4. Conclusions

Table 3 compared partition coefficient of two hexafluorophosphate ionic liquids, obtained by extrapolating the logarithm of experiment K-values to zero ionic liquid concentration, with K_{ow} values other common organic chemicals reported in the literature[15]. [Emim][PF$_6$] and [bmim][PF$_6$] have 1-octanol/water partition coefficient substantially less than 1, while other organic solvents have high 1-octanol/water partition coefficient. The small 1-octanol/water partition coefficient indicates that hexafluorophosphate ionic liquids have low bio-concentration and soil sedimentation tendencies.

Table 3: 1-octanol/water partition coefficients of [emim][PF$_6$], [bmim][PF$_6$] and other organic solvents

Chemical	$\log_{10}K_{ow}$	Chemical	$\log_{10}K_{ow}$
[Emim][PF$_6$]	-1.82	Nitrobenzene	1.84
[Bmim][PF$_6$]	-1.70	Benzene	2.14
Ethanol	-0.284	Chlorobenzene	2.80
Ethyl acetate	0.685	Biphenyl	3.96
1-Pentanol	1.39	Pentachlorobenzene	4.99

Acknowledgement

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